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ADP023628

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TITLE: Army Research Office and Air Force Office of Scientific Research  
Contractors' Meeting in Chemical Propulsion Held in Arlington, Virginia  
on June 12-14, 2006

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# A NEW PARADIGM IN MODELING AND SIMULATIONS OF COMPLEX OXIDATION CHEMISTRY USING A STATISTICAL APPROACH

(Grant Number: ARO-W911NF-05-1-0526)

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## SUMMARY/OVERVIEW:

The computationally accurate and efficient prediction of turbulent reactive flows remains an important research topic for several reasons, one of which is that the modeling of chemistry is still cumbersome, relatively inaccurate, and cannot portray the complex reactions associated with real fuels. To reduce computational costs and enable the description of concurrent reactions from complex fuels containing a multitude of species, a new concept is here proposed that relies on statistical instead of deterministic concepts for modeling chemical kinetics of oxidation reactions. In this new concept, each species has a time scale associated with it, and the goal is to solve only for the significant scales of the problem and model those scales that are not significant. A set of reaction-species mole fractions is considered a vector and the objective is to map this vector into a much smaller multidimensional vector space of base chemical fragments. The goal is to inquire whether such a base can be found for oxidation reactions, and whether one can derive corresponding reaction-coordinate rates for the base that portray the energetics of the system. In essence, there is a functional mapping representing the transformation from the mole fraction PDF of the species to the mole fraction PDF of the base and the interest is not in calculating this functional but its moments (e.g. statistical means, variances, etc.) needed to adequately describe the fragment vector.

## TECHNICAL DISCUSSION

The first step in this new research was to concentrate on finding a potential set of base fragments. The transformation between the vector of the species and the base fragments vector would be represented by a matrix  $[w^c]$  having elements representing the decomposition of each species on the base. Then, the rate of change of the base species is related to the rate of change of the reaction coordinates through the transformation  $[w^c][\chi]$  where the matrix  $[\chi]$  has for elements the stoichiometric coefficients of the initial set of detailed reactions. An example of a detailed kinetic model is the LLNL set of reactions for n-heptane oxidation which involves a total of 160 species and 1540 reactions. The requirement for this reduced set of reactions for the base fragments is that it preserves the heat release, indicating in particular that the heat capacity and heats of combustion must be appropriately modeled. The concept is that although there is a functional mapping representing the transformation from the mole fraction PDF of the species to the mole fraction PDF of the base, if one wants to reduce the complexity of the system, it is not necessary to explicitly know this functional; the goal is to obtain an implicit model based on correlations

resulting from numerical simulations using detailed models, because this implicit model would be much simpler than the explicit one. The following describes a proposed base that is relatively simple, yet potentially accurate.

The guiding idea for the base search is similar to that of group additivity [1]; however, group additivity accounts not only for interactions of a group with its nearest neighbor, but also for interactions with groups not immediately adjacent and for steric effects. The present intention is to only account for the interaction with immediately adjacent groups as the complexity of the correlations in [1] must be decreased if computational efficiency must be improved. Thus, although the idea is very similar to the 'groups' of the group contribution methods of estimating species properties [2], the present focus is on a combination of comprehensiveness, accuracy and relative simplicity in that only first order (compositional) effects are allowed. Examination of alkanes and olefins with a vinyl radical shows that the linearity of thermal properties in carbon (C) number implies that the proper building blocks are 'component radicals' listed in Table 1. Listed in Table 1 are also values of thermodynamic properties and correlations for calculating  $C_p$ , listed here as  $NC_p$  to indicate that these are components. The fitting of the simple formula (much simpler than in [1]) is tested by computing  $C_p/R$  ( $R$  is the universal gas constant) and is plotted in Figs. 1a (alkanes) and 1b (alkenes); the agreement with the correlation is remarkable given its simplicity.

However, for species with double bonds not at the end of the chain or for oxidized species, the simplicity of the component radicals as building blocks no longer rigorously, but only approximately, holds. To calculate combustion energies once either breakup of a hydrocarbon into free radicals or oxidation reactions occur, the assumption is made that one can associate a constant partial energy with all component radicals, independent of the species to which they belong. The data [3-5] show that although this assumption is not entirely correct (when subtracting contributions from  $CH_2$ ,  $CH_3$ , etc.), the variation across species is not that substantial; an average over species is taken. The error in the overall heat of formation for the entire molecule is rather small; two-digit accuracy is normally reached. In Fig. 1c,  $C_p/R$  is plotted for some ethers using the information of Table 1; although there are minor deviations from the data, mostly at low  $T$ , the fits are adequate. The lightest species are not subject to meaningful decomposition. Free radicals occur when a species splits in two (e.g., hydrogen abstraction) by a reaction, forming species with unsatisfied valence bonds; component radicals could also exist as free radicals. Properties of light species and free (component) radicals are given in Table 2. The corrections for the heavier free radicals may be estimated using the increments in hydrogen bond strengths as given in [6]. Figure 1d illustrates  $C_p$  fits for a few free radicals, and good reproduction of the data is shown. Similar fits (not shown) for the light species of Table 2 were equally successful.

Thus, it appears that the base will be formed of 13 component radicals, 11 free radicals and 5 light species. A total of 29 fragments will compose the base, having excluded the final products of combustion (i.e.  $CO_2$  and  $H_2O$ ),  $O_2$  and  $N_2$ , for which the mole fraction can be computed from atomic conservation.

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3. National Institute of Standards and Technology, Chemistry WebBook website; <http://webbook.nist.gov/chemistry>
4. CRC Handbook of Chemistry and Physics, 85<sup>th</sup> Ed., D. R. Lide, Ed.-in-chief, CRC Press, Boca Raton, Fl., 2004 (internet edition)

5. Gas Research Institute website, <http://www.me.berkeley.edu/gri-mech/>

6. Lay, T. H., Bozzelli, J. W., Dean, A. M. and Ritter, E. R., *J. Chem. Phys.*, 99, 14514-14527, 1995

Radical	$\delta h^o$	$\delta h^c$	$\delta h^f$	$a^h$	$b^h$
CH <sub>3</sub> (methyl)	-42.0	714	188	3.137	3.433
CH <sub>2</sub> (methylene)	-20.8	614.3	411	2.784	2.812
CH (methyldiyne)	$\cong -7$	$\cong 507$	$\cong 603$	2.068	3.038
C <sub>2</sub> H <sub>3</sub> (vinyl)	62.5	1212	237	4.432	4.468
C <sub>2</sub> H <sub>2</sub> (CH=CH) <sup>o</sup>	73 $\pm$ 2	1102 $\pm$ 2	not relevant	3.82	3.72
C <sub>2</sub> (C $\equiv$ C, dicarbon)	230	1017	608	2.919	1.796
HC <sub>2</sub> (HC $\equiv$ C, ethynyl)	227	1135	339 **	3.937	2.2515
CO (keto)	-133 $\pm$ 2	260.5	23	2.892	1.531
HCO (formyl)	-124 $\pm$ 3	390.3	167	3.37	2.92
HO (hydroxyl)	-166 $\pm$ 6 ***	-45	204	2.084	1.0945
HOO (hydro-peroxy) <sup>+o</sup>	-205+116/n	-84+116/n	215-116/n	4.194	1.908
OO (peroxy) <sup>*</sup>	-16-13n	-16-13n	not relevant	3.65	2.135
O (ethers) <sup>*#</sup>	-74-13n	-74-13n	323+13n	-1.46	2.44

<sup>o</sup> trans: -2, cis: +2; for a molecule with one or more vinyl also present (i.e., polyene),  $\delta C_p/R$  is increased by 12%; \*\* Alternate value (op. cit. NIST) is 250 from older data; \*\*\* value  $\cong -180$  if combined with CH radical; \* 'n' is the number of carbon atoms in attached radicals; <sup>o</sup> effective n = 1.16 with ring or branched attached radical; # max value  $\Delta n = 2$  for an attached chain, effective n = 3 for a ring with n  $\geq 4$ . If at least one vinyl also present, then add  $\Delta n = +1$ . For a ring with n = 2 or 3, a correction  $\delta h^o \approx 90$  applies. ( $\delta C_p/R$  fit is for ring ethers; for a chain,  $\delta C_p/R \cong 2.5$ ); Note: if the keto (or formyl) radical is attached to oxygen (or hydroxyl), then a correction  $\delta h^o \approx -90$  applies.

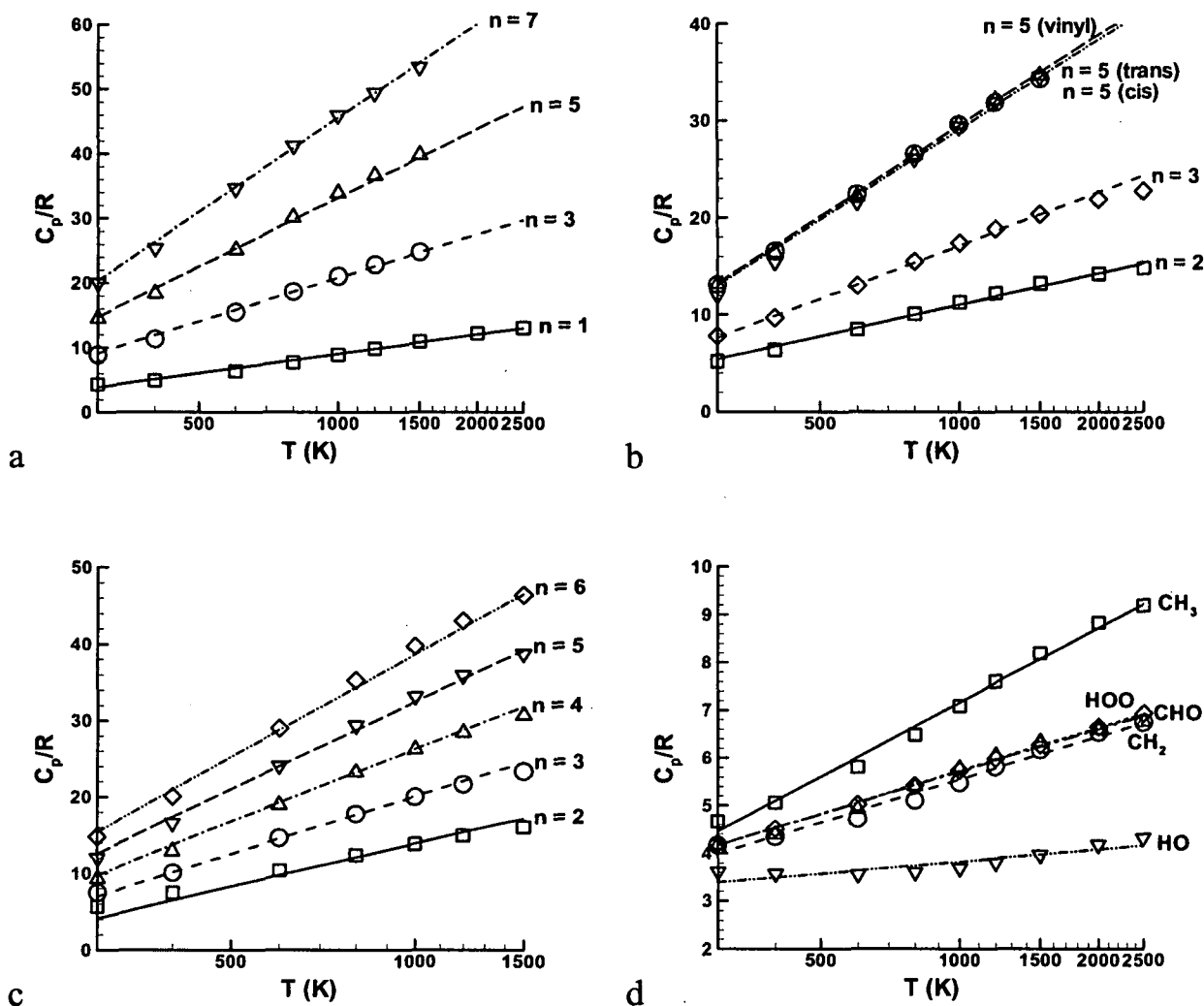
**Table 1. Thermodynamic properties of component radicals. ( $\delta h^o$ ,  $\delta h^c$ ,  $\delta h^f$  heats of formation, combustion, and component-to-free transition, respectively, in kJ/mol; constants  $a^h$  and  $b^h$  for partial molar heat capacity in the form  $\delta C_p/R = a^h + b^h \ln(T/T_o)$ ;  $T_o = 25^\circ\text{C} = 298.15\text{ K}$ )**

Molecule/radical	$h^o$	$h^c$	$a^h$	$b^h$
H <sub>2</sub>	0.0	241.5	3.282	0.400
O <sub>2</sub>	0.0	0.0	3.476	0.5663
N <sub>2</sub>	0.0	0.0	3.388	0.469
C	717	1111	2.50	0.0
H <sub>2</sub> O	-241.5	0.0	3.688	1.217
CO <sub>2</sub>	-393.5	0.0	4.690	1.390
N	473	473	2.50	0.0
H	218.0	339	2.50	0.0
HO	38	159	3.385	0.3637
HOO	10.5	131	4.150	1.307
O	249.2	249.2	2.536	0.0
CO	-110.5	283	3.426	0.4749
HCO	43.1	558	4.154	1.2875
CH <sub>4</sub>	-74.6	802	3.797	4.305
CH <sub>3</sub>	146	902	4.440	2.249
CH <sub>2</sub>	390	1025	3.973	1.3015

CH	596	1110	3.220	0.7136
C <sub>2</sub> H <sub>3</sub>	300	1449	5.1	3.5
HC <sub>2</sub>	566	1474	4.434	1.404
C <sub>2</sub>	838*	1625	4.58	0.0
NO	90.3	90.3	3.533	0.4508
NO <sub>2</sub>	33.2	33.2	4.691	1.151
H <sub>2</sub> O <sub>2</sub>	-136	106	5.269	1.880
C <sub>2</sub> H <sub>2</sub>	228	1257	5.368	2.294
C <sub>2</sub> H <sub>4</sub>	52.5	1323	5.383	4.676

\*Alternate value of 832 from CRC tables

**Table 2. Thermodynamic properties of molecules and free radicals.** ( $h^\circ$ ,  $h^c$  heats of formation and combustion, respectively, in kJ/mol; constants  $a^h$  and  $b^h$  for molar heat capacity in the form  $C_p/R = a^h + b^h \ln(T/T_0)$ .)



**Figure 1.** Plot of  $C_p/R$  vs  $\log(T)$  where  $T$  is in degrees K. Data values are as symbols; lines portray the fit constants. a. alkanes, constants from Table 1; b. alkenes, constants from Table 1; c. ring ethers  $(CH_2)_nO$ , constants from Table 1; d. some free radicals, constants from Table 2.